# The reactions of $N(^2P)$ with $O_2$ and O

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We have studied the kinetics of metastable $N(^2P)$ with atomic and molecular oxygen. The measurements were made in a discharge flow apparatus in which $N(^2P)$ was generated from the energy transfer reaction between $N_2(A)$ and ground state $N(^4S)$ and was monitored either by vacuum ultraviolet resonance fluorescence at 174 nm or else by observing the forbidden $N(^2P-^4S)$ emission at 347 nm. The rate coefficient for $N(^2P)$ quenching by $O_2$ is $(2.2\pm0.4)\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and that for quenching by O is $(1.7\pm0.4)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. One channel of the reaction between $N(^2P)$ and atomic oxygen appears to produce $NO^+$ via a chemi-ionization mechanism.

## I. INTRODUCTION

The reaction between $N(^2D)$ and $O_2$,

$$N(^2D)+O_2\rightarrow NO(v\leqslant 18)+O, \quad (1)$$

is the primary source of NO in the upper atmosphere and of vibrationally excited NO in the disturbed upper atmosphere.[1] Although much less abundant, the more energetic atomic nitrogen metastable, $N(^2P)$, can react with molecular oxygen to produce NO with significantly more internal energy,

$$N(^2P)+O_2\rightarrow NO(v\leqslant 26)+O, \quad (2a)$$

$$N(^2P)+O_2\rightarrow NO(v\leqslant 9,\ J\sim 80\text{–}120)+O. \quad (2b)$$

While reaction (1) is well characterized in most regards,[2–9] published values of the total rate coefficient for reaction (2) vary by a factor of 2.[4,5,10,11] The products of reaction (2) have not been characterized at all, although Rawlins *et al.* have suggested that highly rotationally excited NO is the principal product.[9]

The reaction between $N(^2P)$ and atomic oxygen,

$$N(^2P)+O(^3P)\rightarrow N(^2D,^4S)+O(^3P,^1D) \quad (3a)$$

$$\rightarrow NO^+ + e^-, \quad (3b)$$

is even more poorly characterized. Only one experimental measurement of the rate coefficient for reaction (3) has been published,[10] although the rate coefficient has been estimated from laboratory[12] and aeronomic[13] observations. These estimates differ by nearly an order of magnitude. Theoretical considerations apparently favor channel (3a) over (3b),[14,15] but experimental support is lacking.

This paper describes the measurements of the rate coefficients for $N(^2P)$ quenching by atomic and molecular oxygen. In addition we present evidence in support of channel (3b).

## II. EXPERIMENT

The apparatus is a modification of one we have used previously in a number of other studies.[8,16,17] It consists of a 2 in. i.d. flow tube pumped by a Leybold–Heraeus Roots blower/forepump combination capable of producing linear velocities up to $5\times10^3$ cm $s^{-1}$ at a pressure of 1 Torr. The flow tube design incorporates separate source, reaction, and detection sections clamped together with O-ring joints (see Fig. 1).

The $N(^2P)$ was made in the upstream section of the flow reactor by adding a flow of nitrogen atoms to a flow containing metastable $N_2(A\ ^3\Sigma_u^+)$.[16] A low power, hollow-cathode dc discharge through a flow of argon produced metastable $Ar^*(^3P_{0,2})$. Downstream from this discharge, molecular nitrogen was mixed with the Ar*, and the resulting energy transfer reaction between these two species ultimately made $N_2(A)$.[18,19]

Atomic nitrogen was generated in a microwave discharge through a flow of nitrogen and argon in an 8 mm i.d. fixed point injector. Atomic nitrogen number densities were determined from NO titrations using procedures we have detailed previously.[20,21] To ensure complete conversion of $N_2(A)$ to $N(^2P)$ prior to the reaction zone, we monitored the spectral region between 250 and 350 nm using a 0.5 m monochromator placed ~10 cm downstream from the N-atom injector. We adjusted the N-atom flow to be as small as possible while still ensuring complete removal of the Vegard–Kaplan band emission, $N_2(A\ ^3\Sigma_u^+-X\ ^1\Sigma_g^+)$, diagnostic of $N_2(A)$. This procedure minimized both $N(^2P)$ losses from N-atom quenching and $N(^2P)$ production from N-atom recombination.[23]

Molecular oxygen entered the flow tube through a movable loop injector consisting of a 0.25 in. diam length of stainless steel tubing capped with a perforated Teflon loop epoxied into its downstream end. The zero of the scale relating the distance between the injector and the detection region was calibrated by measuring the point at which the scattered light from the resonance fluorescence lamp suddenly increased as the injector was moved into the detection region.

To measure $N(^2P)$ quenching by atomic oxygen, we added O-atoms through a downstream fixed injector. The atomic oxygen was produced in the injector by titrating N atoms with NO. A microwave discharge through a flow of nitrogen in argon produced the N-atoms in the upstream end of the injector.

Mass flow meters monitored the flow rates of most gases, although rotameters were used for a few minor species. All flow meters were calibrated by measuring rates of

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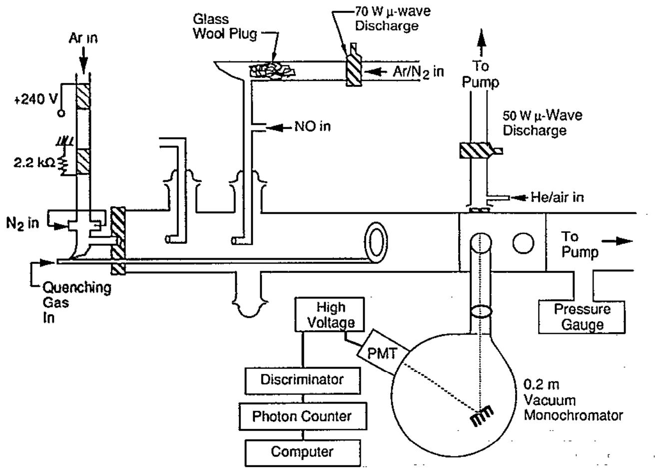

FIG. 1. Schematic of discharge-flow apparatus for studying $N(^2P)$ quenching kinetics.

increase in pressure with time into 6.5 or 12 ℓ flasks, using appropriate differential-pressure transducers (Validyne DP-15) which had themselves been calibrated with silicon oil or mercury manometers. Typically the flow rates for argon or helium, nitrogen, and quencher were 2000–5000, 50, and 0–120 $\mu$mol $s^{-1}$, respectively. The total pressure was generally 1–3 Torr, and the flow velocity was 1000–3500 cm $s^{-1}$.

Metastable $N(^2P)$ number densities were measured by resonance–fluorescence.[8,22] Because the resonance lines of both $N(^2D)$ and $N(^2P)$ originate from a common upper state, one of the lines must be removed from the lamp so that the two metastables can be distinguished from each other. A suprasil window between the lamp and the flow reactor passed the 174 nm emission for $N(^2P)$ pumping, but rejected the 149 nm emission absorbed by $N(^2D)$. The combination of a 0.2 m vacuum monochromator, a photomultiplier with a CsI photocathode (120–185 nm sensitivity), and a photon-counting rate meter measured the resonance–fluorescence intensities in the flow tube.

## III. RESULTS

### A. $N(^2P)$ quenching by $O_2$

With the $N_2(A)$ off, some $N(^2P)$ still persisted in the flow reactor. This $N(^2P)$ was generated by transfer from $N_2(A)$ created by N-atom recombination.[23] The contribution to the total $N(^2P)$ signal from this secondary process, therefore, had to be subtracted to obtain unequivocal measurements. As a result, we monitored the decay of $N(^2P)$ as a function of added quencher both with the $N_2(A)$ on and with it off. The difference between the two sets of measurements, then, represents the quenching of the directly introduced $N(^2P)$. For the measurements on $O_2$ quenching this correction was small, generally $<10\%$.

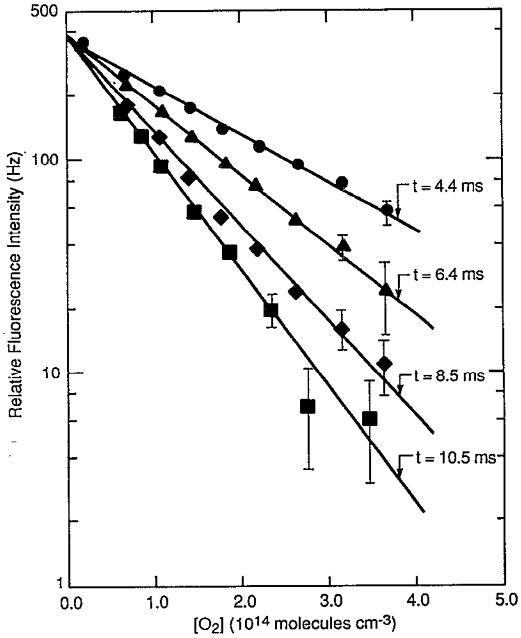

FIG. 2. Decay of $N(^2P)$ as a function of added molecular oxygen at four different reaction times.

Rate coefficients were determined from measurements of the change in the natural log of the metastable nitrogen number density as a function of number density of added quenching reagent with fixed reaction distance $z$, or time, $z/\bar{v}$,[8]

$$-\frac{d\ln[N\,^2P]}{d[Q]}=0.62\;k_Q z/\bar{v}=\Gamma(z), \qquad (4)$$

where the factor of 0.62 is a fluid mechanical correction needed to account for a parabolic velocity distribution in the flow tube.[24] The decay coefficient, $\Gamma$, requires corrections to the reaction distance, $z$, to account for imperfect mixing at the injector. Thus, one must measure decay coefficients at several different distances with all other conditions fixed, and then determine the rate coefficient from a plot of $\Gamma$ vs $z$.

Figure 2 shows some typical decay plots for $N(^2P)$ quenching by molecular oxygen. The slopes of the lines in Fig. 2 are the decay coefficients at different reaction times. Plotting the decay coefficients as a function of reaction time, as shown in Fig. 3, corrects for imperfect mixing at the injector. The slope of the line in Fig. 3 is the rate coefficient for reaction (2) and the intercept is the effective $O_2$ mixing time in our reactor. Our results indicate that the rate coefficient for $N(^2P)$ quenching by molecular oxygen is $(2.2\pm0.4)\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The error bars are a root-mean-square (rms) combination of the statistical uncertainty ($2\sigma=14\%$) and the systematic uncertainty, 10%.

Our result agrees, within the limits of quoted error, with Husain *et al.*[5] measurement of $(2.6\pm0.2)\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and the more recent measurement of Phillips *et al.*,[11] $(1.8\pm0.2)\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Iannuzzi and Kaufman's[4] value of $(3.5\pm0.5)\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ is somewhat larger than a consensus value based upon the other three sets of measurements.

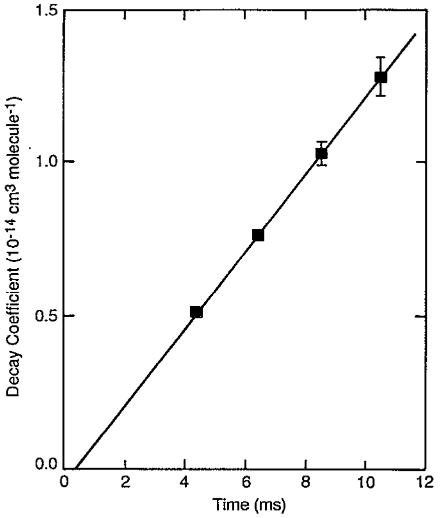

FIG. 3. Decay coefficients for $N(^2P)$ quenching by molecular oxygen as a function of reaction time.

### B. $N(^2P)$ quenching by O

The procedure for measuring $N(^2P)$ quenching by O was similar to that given above for the quenching of $N(^2P)$ by $O_2$. The decay of $N(^2P)$ was monitored as a function of added NO with the $N_2(A)$ discharge on and with it off. NO quantitatively converts N atoms to O, so the flow of O into the reactor will equal the flow of NO titrant added to the injector sidearm. The difference between the two decay curves was taken to represent the true rate of $N(^2P)$ quenching by O-atoms. Figure 4 shows two decay plots and their associated difference plot. Even though neither of the two raw decays are linear on the semilog plot, the difference between them is. The slope of this difference decay is the decay coefficient for quenching $N(^2P)$ by O as given in Eq. (4).

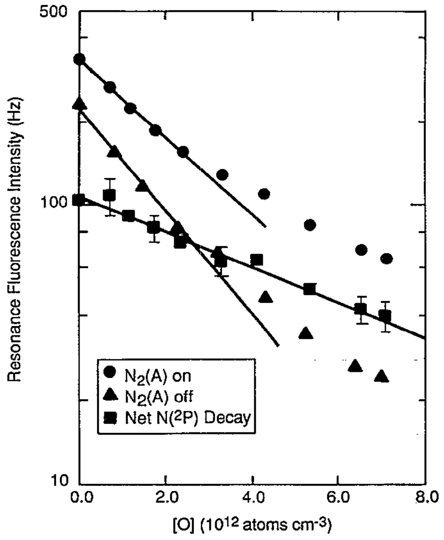

FIG. 4. Decay of $N(^2P)$ resonance–fluorescence intensity as a function of added atomic oxygen.

The N-atom number density required to make sufficient O for these measurements was several times greater than that required just to produce $N(^2P)$. Thus, the $N(^2P)$ generated from N-atom recombination was a much larger fraction of the total, as much as two-thirds of the total $N(^2P)$. Because the NO titration reaction reduced overall N-atom number densities, the background component decreased considerably, and nonexponentially, as the added NO increased.

Because the fixed injector does not give perfect mixing, we next determined a decay coefficient for $N(^2P)$ quenching by $O_2$ added through the same injector under otherwise similar flow conditions. The rate coefficient for O-atom quenching of $N(^2P)$ is then the ratio of the two decay coefficients times the previously determined rate coefficient for $N(^2P)$ quenching by $O_2$. Our measurements show that the ratio of the two rate coefficients is $7.6 \pm 1.1$, making the rate coefficient for $N(^2P)$ quenching by O $(1.7 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The $N(^2P)+O$ rate coefficient has been estimated by Golde and Thrush[12] to be quite fast, $k_3 \sim 7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and by Young and Dunn[10] to be somewhat slower, but still fast, $k_3 \sim 1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This is one of the few cases for which $N(^2P)$ quenching is reported to be faster than the corresponding quenching reaction with $N(^2D)$ ($k = 1.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).[17]

### C. Chemi-ionization from $N(^2P)+O$

Several groups have suggested that the interaction between $N(^2P)$ and O might be a chemi-ionization reaction producing $NO^+$,[13] although others have argued on theoretical grounds that this mechanism is not likely.[14,15] If it is a chemi-ionization reaction, this would explain the fast quenching of $N(^2P)$ by O. We tested for ionization by inserting electrodes into our flow reactor and measuring the resultant ion current. The electrodes consisted of a 1 in. diam loop centered along the flow tube axis upstream from the O-atom injector and a similarly sized circular electrode covered with nickel screen 10–20 cm downstream from the injector. The upstream electrode was biased positively while the downstream electrode, the collector, was at ground potential.

Figure 5 shows the variation in the collector current as a function of the potential difference between the two electrodes. The current rises quite steeply at low voltages, then levels off as the collector becomes saturated, and finally rises again as energetic ions and electrons in the gas begin to ionize the background argon.

Figure 6 demonstrates that the current collected in the plateau region (~75 V) varies linearly with the number density of $N(^2P)$. Additional measurements also showed that the current tracked linearly with the O-atom number density. In the absence of either $N(^2P)$ or O atoms, the ion current vanished. This evidence presents a strong case that chemi-ionization is at least one channel of the $N(^2P)$ plus O reaction. Our apparatus was not equipped with a mass spectrometer to identify $NO^+$ ions unequivocally, however, they seem the most likely candidate.

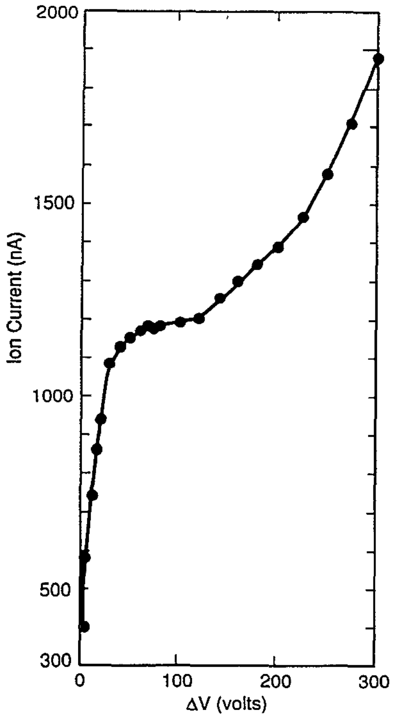

FIG. 5. Ion collection as a function of potential difference across electrodes.

The electrodes were not designed to collect the total ion current generated in the flow reactor. As a result, the magnitude of the ion current can only be used to determine a lower limit to the efficiency of the chemi-ionization channel. We estimate that at least 10% of the N($^2P$) atoms removed from the reactor are converted to ions. The true efficiency could be much higher than this.

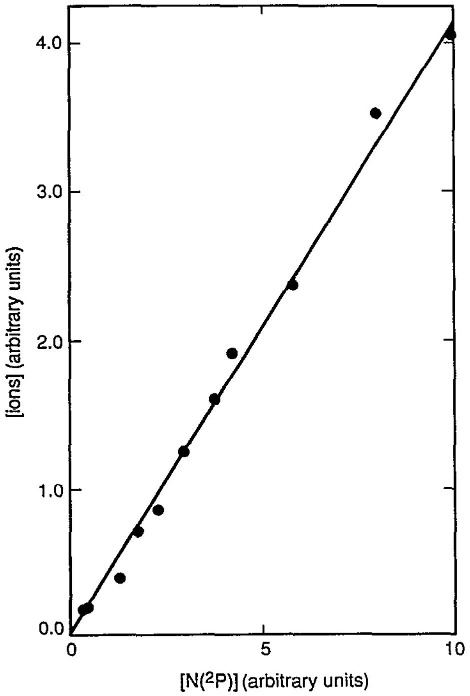

FIG. 6. Relationship between saturated ion current and [N($^2P$)] for fixed [O].

## IV. DISCUSSION

The reaction between N($^2P$) and O atoms is exoergic by ~0.3 eV for the channel to make $NO^+$. Any other likely ions in the reactor would require somewhat more energy to produce. Support for the chemi-ionization channel comes from the experiments of Gatz *et al.*[25] They observed ion production when they added oxygen atoms to active nitrogen. By varying the potential between their electrodes, they were able to measure the mobility of the ions produced in their reactor. The mobility was exactly that which would obtain for $NO^+$.

The principle removal mechanism for $NO^+$ ions is dissociative recombination with thermal electrons and the branching ratio for N($^2D$) production in $NO^+$ dissociative attachment is essentially unity.[26] Thus, if reaction (3b) is indeed the primary channel for N($^2P$) quenching by atomic oxygen, then the effects resulting from N($^2P$) production in the upper atmosphere would be indistinguishable from those resulting from N($^2D$) production. This is because N($^2P$) atoms will be predominantly converted to N($^2D$) either by dissociative recombination of $NO^+$ with electrons, reaction (3b), or via radiation to N($^2D$) at 1040 nm.

The principal processes for N($^2P$) removal at altitudes above 100 km are quenching by O atoms and, above 180 km, radiative decay. N($^2P$) radiates both in the infrared at 1040 nm to N($^2D$) and in the ultraviolet at 346.6 nm to N($^4S$). The transition probability of the 1040 nm transition is 16 times that of the 346.6 nm transition.[27] Thus, 94% of the N($^2P$) that radiates will end up as N($^2D$).

Overall N($^2D$) production rates in an aurora are much larger than those for N($^2P$) (Ref. 28) and N($^2P$) quenching by O atoms is an order of magnitude faster than is quenching by $O_2$. Thus, only in a deeply penetrating aurora should NO($v$) production from the reaction of N($^2P$) with $O_2$ be important.

Rawlins *et al.*[9] have observed high $J$ rotational bandheads in the infrared spectrum of NO($v$,$J$) produced in the interaction of discharged nitrogen with $O_2$. They speculated that these bandheads arose because a large fraction of the exoergicity of reaction (2) ended up as rotational energy in the product NO. They hypothesized that the rotationally hot NO($v$,$J$) could lead to significant emission in infrared bandpasses generally thought to be devoid of radiation.

Some support for the production of NO($v$,$J$) bandheads in a disturbed atmosphere issues from the interferometric observation of an aurora by Espy *et al.*[29] They observed several emission peaks to the blue of the main NO($v$,$J$) emission band. These peaks matched the location of the rotational bandheads observed by Rawlins *et al.*

Vallance Jones and Gattinger[30] have discussed how the mean altitude of an aurora can be determined by comparing the emission intensity of the N($^2P$–$^2D$) emission at 1040 nm to that from the $N_2$ first-negative system,

$N_2^+(B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+)$, or some other radiative feature known to be in fixed ratio with the $N_2^+(B-X)$ emission. The $N_2^+(B)$ emission intensity is a measure of the ion-pair production rate in an aurora. The primary production process for $N(^2P)$ is dissociative excitation of $N_2$ by the electrons.[28] This process has a cross-section energy dependence similar to that of $N_2^+$ production, so the ratio of excitation rates of $N(^2P)$ to $N_2^+$ should remain relatively constant over the range of typical auroral excitation conditions. $N_2^+(B)$ has a radiative lifetime of 65 ns and will not suffer quenching at any auroral altitudes. Any diminution in the ratio of emission intensities of $N(^2P)$ to $N_2^+(B)$, therefore, will be related to the local O-atom number density. The local altitude of the observed emission can be determined using a model atomic oxygen altitude profile.

Zipf *et al.*[13] used a variation of this approach to estimate the rate coefficient, $k_3$. They determined changes in the $N(^2P)$ to $N_2^+(B)$ intensity ratio as a function of altitude from data taken during a rocket flight. Combining their intensity ratio observations with an assumed O-atom number density profile allowed them to infer a value for $k_3$ of $1\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, in reasonable accord with our direct measurement.

## V. SUMMARY

We have determined rate coefficients for $N(^2P)$ quenching by $O_2$ and O to be $(2.2\pm0.4)\times10^{-12}$ and $(1.7\pm0.4)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Our observation of ion production in the $N(^2P)$/O atom system indicates chemi-ionization to form $NO^+$ is probably a significant reaction channel in this system, in contradiction to theoretical arguments.

## ACKNOWLEDGMENTS

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